LA-UR-21-28132

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Intended for:	Report
Issued:	2021-08-13

A novel approach to characterize the full spectrum and radiative properties of aerosols

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ABSTRACT

Organic aerosols play a significant role in the absorption and radiative budget of the atmosphere, but current modeling approaches do not adequately capture the photo-chemical and oxidative bleaching that occurs during their lifetimes. Most climate models inaccurately assume constant optical properties of these particles, therefore leading to errors in their predictions. In this study we present an approach to better parameterize the optical properties of atmospheric aerosols, including brown carbon (BrC). Using thin-film spectrometry, the full spectrum of reflectivity and emissivity was used to calculate the complex refractive index for multiple species of organic aerosols. This is in contrast to previous techniques which only probe single wavelengths. Since BrC is a complex molecular mixture, we initially focused on single species absorption using four molecular surrogates. Dye-doped polyacrylic-acid thin-films were prepared on glass slides and compared to an aerosolized collection method. Verification of the collection method will open the door to characterizing the complex refractive index of smoke and ambient aerosol.

I. INTRODUCTION

Organic aerosols, such as brown carbon (BrC), are one of several driving factors which determine Earth's radiative balance. The ability of these aerosols to both scatter and absorb incoming solar radiation influences global climate by changing the exposure to solar radiation[1]. We cannot predict Earth's RF without properly understanding how the sun's radiation interacts with the chemical species in our atmosphere. Feng et. al. [2013] showed that BrC accounts for 19 % of the total atmospheric absorption, caused by anthropogenic aerosols, but current methods for capturing its effects do not accurately represent the physical and chemical changes which occur during atmospheric transport[2]. Unlike similar aerosols such as black carbon, both photo-chemical and oxidative bleaching has been observed in BrC samples. This leads to significant changes in photo-chemical processes and a reduction in absorption; showing the dynamic nature of the effects aging has on its optical properties[3]. These processes are not properly implemented into current climate models and instead the optical properties of BrC, among other atmospheric aerosols, are often assumed to be fixed. (Need to cite a model here that assumes constant properties) In this work we present new methods for measuring the complex refractive index of aerosol species. This will allow for greater accuracy in parameterizing the changing properties using a full spectrum of wavelengths (190 nm to 1100 nm).

Four organic dyes (sunset yellow, para red, fluorescein sodium salt, and nigrosin) were used in place of BrC during this study because of their molecular structures and BrC like absorption behavior. Using the dye samples, thin-films were created on glass slides using both chemically doped poly-acrylic acid (PAA) solutions and direct collection of aerosolized dyes onto pre-made PAA films. We measured the reflectance and transmittance's spectra of both sample preparation methods, and the similarity between their measured spectra and comparisons to model predictions was used to validate the direct collection method. The aerosolized collection method has the potential to be used with a wide array of aerosol species as it does not require the sample to be dissolved in the PAA solution - and is instead measured as a separate layer. Collecting the sample as an aerosol also allows for further analysis to be done, such as artificial aging caused by exposure of the slide to ozone. Correct implementation of this procedure has the ability to greatly expand the measurement capabilities for determining the absorption spectrum of aerosols.

II. METHODS

A. Current Methods

When working with ambient aerosols, the most commonly used photo-acoustic devices (such as the CAPS, PASS, and PAX systems) are only able to measure absorption at a single wavelength. This wavelength limitation leads to severely incomplete data of the full absorption spectra of aerosols. Other methods such as the filter based aethalometer, which measures attenuation caused by black and brown carbon with the use of a filter strip, are often subject to biases which can skew their results. Optical inconsistencies in the filter paper along with the potential for the device to be overloaded with aerosol both contribute to errors in filter based measurements. Discrepancies propagated by these measurements necessitate that new methods be explored to capture the full absorption spectrum of aerosol samples.

B. New Methods

Two new methods were used during this study to determine the spectra of the three organic dyes of interest, both of which relied on thin-film spectrometry. The measurement of thin-films involves the creation of uniformly thin layers of solutions on glass slides using a spin coater (Ossila, Sheffield, UK). We used a mix of poly-acrylic acid (PAA) and water for the film, as it adhered to substrate but was still viscous enough to be evenly distributed by the spin-coater. Once the films were created, we used a Filmetrics F10-RT-UV spectrometer (San Diego, CA) to obtain the a wide spectrum of light reflectance and transmittance (190 nm to 1100 nm). This spectral measurement is then used to calculate the wavelength dependent complex refractive index, film thickness, and film non-uniformity of the sample. Table 1 summarizes the measured thicknesses of different solutions of PAA and water, showing that the concentration of PAA affected the thickness of the slides in a predictable way; this allowed for better initial guesses to be made when modeling the thicknesses of the sample dye slides. Taking measurements of these slides also provided us with an averaged RI metric for poly-acrylic acid, which was used during analysis.

Poly-acrylic Acid Solutions		
Ratio of PAA to H20	Thickness [nm]	Non-uniformity [nm]
1:1	2092	51.0
1:1	2178	32.0
1:2	1111	53.0
1:2	1108	47.0
1:3	529	48.0
1:3	513	37.0

Table 1: Thicknesses of slides with varying concentrations of PAA

1. Direct Doping

The first method of slide creation relied on the direct chemical doping of PAA solutions with the four dye samples. All PAA solutions used throughout these experiments were 65% water and 35% PAA by weight. In order to make the dye doped solutions, the dyes were directly dissolved in the PAA solution. When working with the sunset yellow and nigrosin dyes, this could be done directly with a solution of water and PAA (3:1 $H_2O : PAA$) since both dyes are water soluble. In a small beaker, 2 mL of the $H_2O : PAA$ solution was mixed with increasing amounts of dye; the concentrations of which are found in table 2. After ensuring the dye was completely dissolved, a pipette was used to inject 1 mL of the solution onto the center of the slides held in the spin coater. The solution was deposited at 100 rpm and after which the rotations were promptly turned up to 3000 rpm. The slides were spun at 3000 rpm for 55 seconds at this speed to ensure an even coating across the surface.

Sunset Yellow		
Sample Number	mg of PAA	mg of dye
1	252	50.5
2	252	25.3
3	252	30.0
4	252	75.0

nigrosin		
Sample Number	mg of PAA	mg of dye
1	252	0.7
2	252	1.5
3	252	4.0
4	252	10.0
5	252	10.0

Table 2: Concentrations of Sunset Yellow and nigrosin in PAA solutions

Fluorescein-sodium-salt required additional steps due to its low water solubility. We used a combination of acetone and water to dissolve the fluorescein dye powder. We then used two different methods in order to create the film samples. The first was identical to the method used with the previous dyes, but with the introduction of acetone into the doped solution. Using a 1:1:1 (*PAA* : H_2O : *Acetone*) solution directly doped with dye, 1 ml was spun onto the slides spinning at 3000 rpm for 55 seconds. The second method involved creating two layers of solution on the sample slides. First, 1 ml of a 2:1 H_2O : *PAA* solution was injected onto the spin coater, and on top 1 ml of a filtered-fluorescein solution (5 ml H_2O, 5 ml acetone, 65 mg fluorescein dye) was promptly injected on top. The result was a two layer stack on the slides. Table 3 summarizes the mixtures used during this step; the mass of PAA is unknown because we filtered the dye solution removing undissolved mass.

Fluorescein-Sodium-Salt: Doped		
Sample Number	mg of PAA	mg of dye
1	252	15.0
2	252	25.0
3	252	30.0

Fluorescein-Sodium-Salt: Layered	
Sample Number	mg of Dye
1	16.3
2	16.3
3	16.3

Table 3: Concentrations of Fluorescein-sodium-salt in PAA solutions

2. Aerosol Collection

The second method of slide preparation relied on the direct collection of aerosol particles. When making these, the first step was to create a film-layer of pure water-PAA solution on the slides to give the aerosols something to stick to. For this process, we used a solution of 2:1 (water:PAA). Aerosolization of the dyes was done with a simple set-up comprised of an atomizer with 1/4" tubing connecting it to a stationary outlet which injected the aerosols 40 mm above the slides at a flow rate of 2 L/min, shown in Fig. 1.
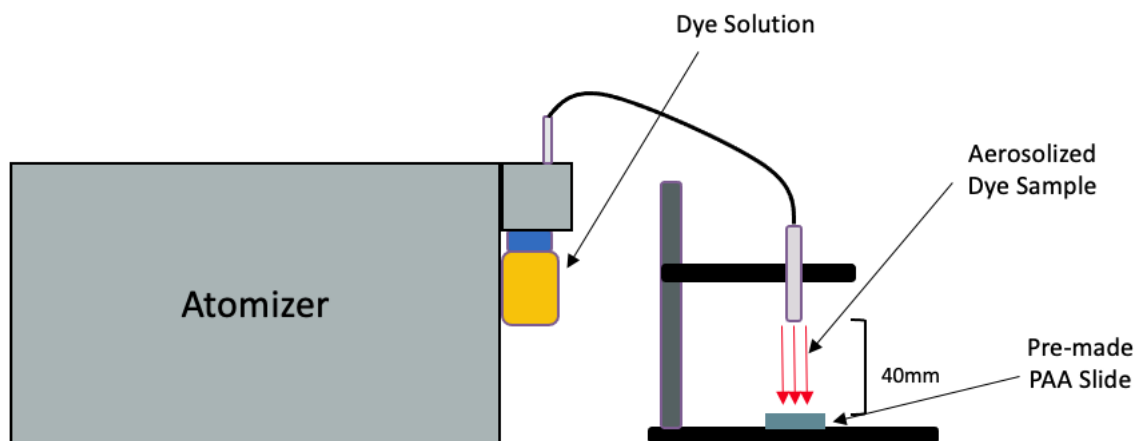

FIG. 1. Atomizer set-up used during aerosol collection process

After spinning the pure water-PAA solution onto the slides, they were quickly moved under the atomizer set-up to begin the collection process where they were exposed to the stream of aerosolized dyes for 20 seconds. While the slides were being exposed to the atomized samples, it worked best to move them side-to-side very slightly to prevent the build-up of particles and improve the uniformity of the resulting layer. This process resulted in small areas of collected aerosols, rather than a layer that covered the entire slide (as was the case with the doping method), a difference that is highlighted below in Figure 2.

C. Slide Analysis

After sample creation, analysis of their spectra was performed using the spectrometer. Full spectrum analysis was performed by measuring the reflectivity and emissivity from 250-850 nm wavelengths of light, as well as the film thickness of the dye layers. The Filmetrics provided
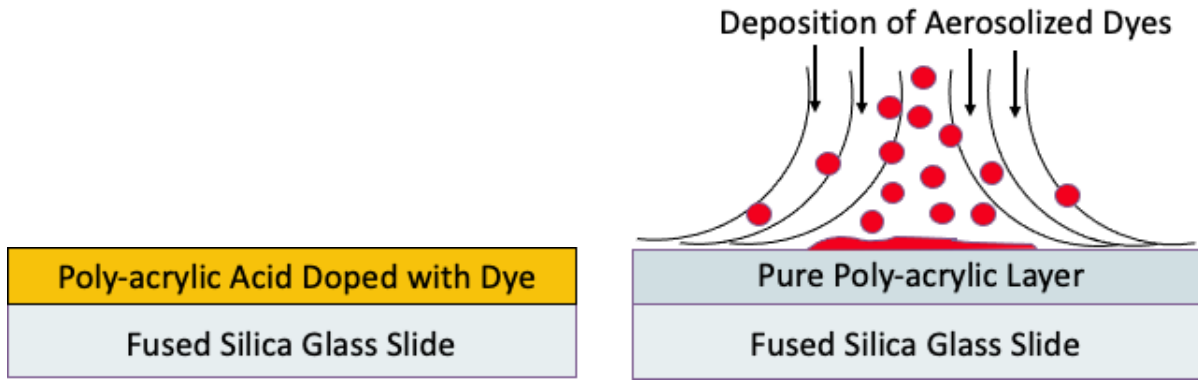
FIG. 2. Slides created with the doping method compared to those created with the direct collection of aerosols

software was then able to model the refractive index based on the interference pattering in the spectra. Wavelength-dependent refractive index values could be calculated using several different functional forms, but for the measured spectrum of the dyes, the 'no-model' was the only option that could correctly capture the interference patterns in the reflection and transmission caused by the dyes. The 'no-model' used a piece-wise linearly interpolated curve, which was needed to capture the complex absorption resonances of the samples. This in turn led to a degradation in the quality of the predicted real component of the refractive index, which will be addressed in future developments. Inputs to the software included initial guesses for the thickness and non-uniformity of the slides, as well as bounds on those to parameters.

1. Doped Slide Analysis

When working with the doped slides, the spectrometer modeled only the single layer of PAA solution doped with dye. This necessitated that the results from these samples be post-processed in order to calculate the RI of the dye alone; since the PAA solution would also be contributing. Using the Lorentz-Lorenz volume mixing relationship described by Liu, Duam 2008, the RIs of the two materials could be separated. After converting the masses of the dye and PAA in the slide solutions to volume fractions using their densities (found in table 4), equations 1 and 2 were used to calculate the RI of the dye based on its concentration in the solution.

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$$r_e = \frac{k_e - 1}{2 + k_e} \tag{1}$$

Where k_e is the effective refractive index and r_e is the effective specific refraction for the dye component of the mixture.

$$k_{dye} = \frac{-2(r_e - v_{PAA}(\frac{k_{PAA} - 1}{k_{PAA} + 2})) - v_{dye}}{(r_e - v_{PAA}(\frac{k_{PAA} - 1}{k_{PAA} + 2})) - v_{dye}} \tag{2}$$

Where k_{dye} and k_{PAA} are equal to the complex refractive index components and v_{dye} and v_{PAA} represent the volumes of the dyes and PAA, respectively.

Densities [g/ml]	
Sunset Yellow	0.5
Nigrosin	0.75
Fluorescein Sodium Salt	1.6

Table 4: Density values of dye powders

2. Aerosolized Slide Analysis

Analyzing the slides created via the aerosol deposition process required a modified procedure due to the PAA and dye layers being separate. This allowed for us to directly measure the RI of the dye samples since no mixing with the PAA solution occurred; this is another advantage to this method as it does not rely on any kind of post-processing of the resultant RI. When modeling these samples, we first defined the PAA layer using the previously collected averaged RI data, and then created a second layer representing the dye. The initial guess inputted to the software for the RI of the dye layers were the averages of the doped samples' RI information for each dye respectively. This allowed for a higher level of accuracy in the model when capturing the reflection and transmission of the aerosolized slides. These methods of analysis were also used for determining the RI information of the layered fluorescien samples; because although that process involved no aerosol collection, it resulted in slides with two distinct optical layers.

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III. RESULTS

Results from our experiments showed promise for both the doping and direct collection methods of measuring aerosol spectra. When compared to model predictions[4] both methods produced similar results for the measured complex component of the refractive index. The following figures display the full spectra analysis that we obtained compared to predicted values, the shaded regions representing the maximum and minimum values calculated for each data series.
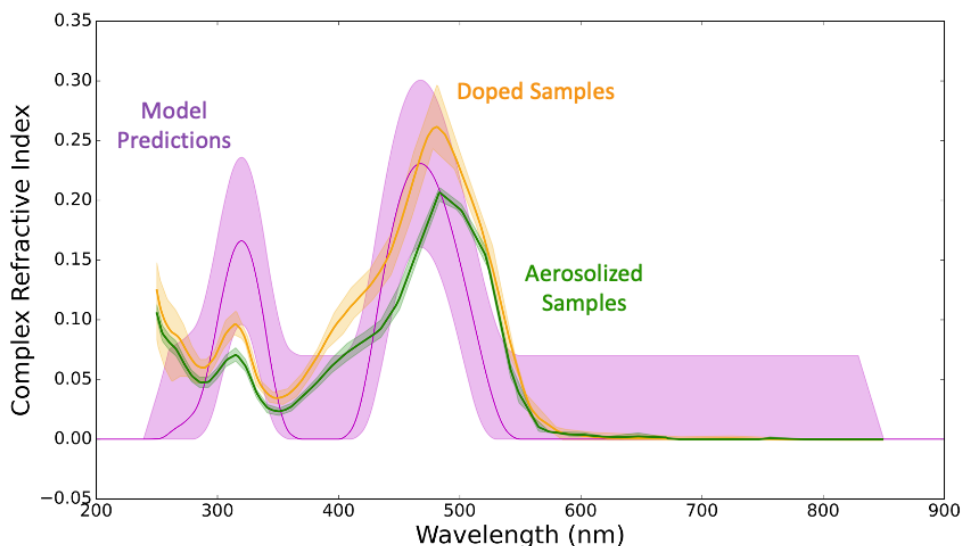
A. Sunset Yellow

FIG. 3. Complex results - sunset yellow

Sunset yellow's results were the most similar to the predicted refractive index values for both the aerosolized and doped methods. We believe this was due to a combination of sunset yellow's high water solubility as well as the ease at which the dye could be collected when aerosolized. Having high water solubility ensured that the doped samples were consistent and did not contain any small undissolved dye particles that could interfere with the creation of the thin films. More consistent thin films resulted in consistent measurements with the spectrometer, since the resultant thickness was highly uniform. It also ensured that no secondary chemicals had to be used to help dissolve the dye - as was the case with fluorescien sodium salt's use of acetone. When aerosolized, sunset yellow produced uniform collection spots on the glass slides; shown in the figure by the very

small range of minimum and maximum values on the aerosolized curve. This again improved the measurements made with the spectrometer, allowing for more consistent thicknesses on the slides and better parameterizations of the software's RI models.

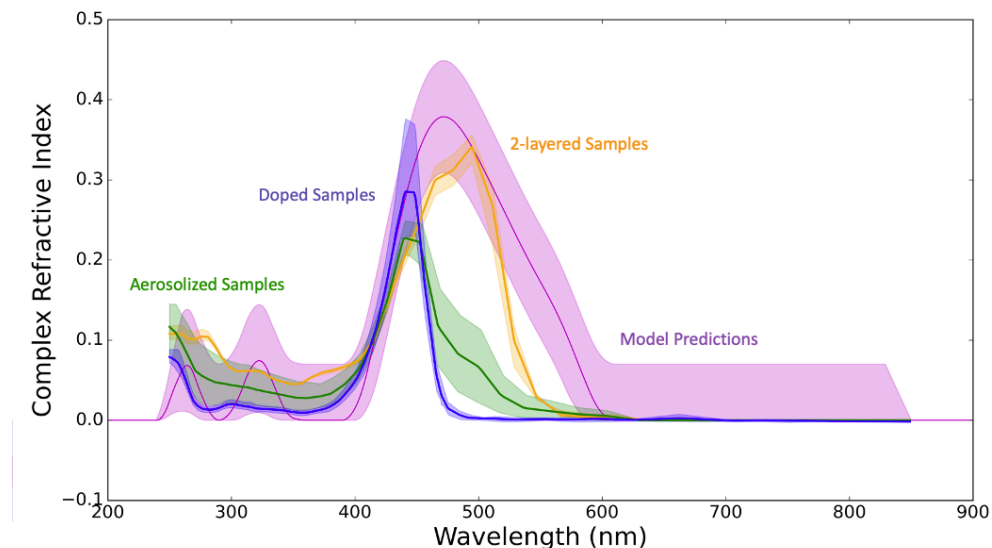## B. Fluorescein Sodium Salt

FIG. 4. Complex results for fluorescein sodium salt

Fluorescein samples provided insight into how the solubility of certain components of the dyes can significantly impact the resultant measured RI. As can be seen in the figure, there is an additional 2-layer samples curve present on this figure, which corresponds to the two step injection method using acetone described in the methods section; while the 'doped samples' curve correspond to the slides created with the 1:1:1 PAA:H2O:acetone mixture injected on a single layer. These results, along with observations made when working with the dye, suggested that only the green/yellow component of the dye is optically active when water is used as the solvent. This can help to explain the differences between the doped and aerosolized samples compared to the layered samples and model prediction curves. Since the layered samples used two distinct layers - with one comprised of dye solution, acetone, and water only - it was able to best capture the actual RI of the dye; as these results are very similar to the model predictions. However, when the 1:1:1 solution was used, this was not the case. We believe this was due to other chemical reactions occurring between the PAA and acetone that rendered the acetone unable to fully dissolve

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the dye powder. Similarly, the solution used to aerosolize the dye was comprised of only water and fluorescein, giving it a RI profile much more similar to the doped samples.
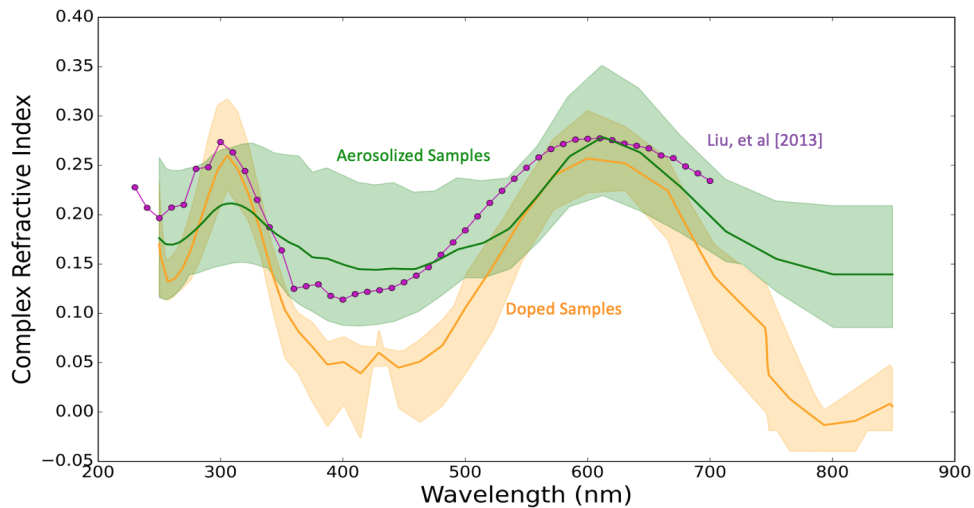
C. Nigrosin

FIG. 5. Complex results - nigrosin[5]

Results of the nigrosin slides suggested that the aerosolized samples were able to capture the complex RI more accurately than the doped method. For this sample, we used data from Liu, et al [2003] to use as a baseline for our results, as we did not have model predictions for this dye. Agreement between the aerosolized slides and literature values highlight the promise of this method, and show that for some aerosols direct collection can provide more accurate results than directly doping solutions. This finding is significant because most atmospheric aerosols of interest (such as black and brown carbon) will only be able to be captured using the aerosol method.

IV. DISCUSSION

Both of the new methods used during this study show promise for characterizing the full spectrum absorbance of atmospheric aerosols. Results generally agreed with model predictions and previous literature findings, showing that the use of thin-film spectrometry has great potential for use with a wide array of aerosol samples. Future work will focus primarily on the improvement of the impaction process used during the aerosolization method. The use of 3D printed slide hold-

ers under the aerosolized stream of the atomizer could prove useful in providing more reliable and uniform areas of dye deposition; therefore improving the uniformity of the resultant samples. Modeling of the aerosol impaction would provide insight into the sizing of the deposited aerosol based on the flow rate of the atomizer, which could be used to better parameterize the process. Future work will also involve deploying these methods in the field. This will allow for better spectral measurements of both ambient urban pollution and larger emission sources such as wildfires.

V. ACKNOWLEDGMENTS

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